

## X-ray Propagation and Diffraction in Distorted, Anisotropic, Dielectric and Magnetic Crystals

BY T. J. DAVIS

*CSIRO Division of Materials Science and Technology, Private Bag 33, Rosebank MDC, Clayton, Victoria 3169, Australia*

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### Abstract

The interaction of X-rays in distorted anisotropic crystals is derived using a semi-classical approach based on Maxwell's equations. The X-ray wave is represented by a vector potential that is coupled to the charge and the magnetic moments of the electrons in the crystal by scattering factors obtained from non-relativistic quantum theory. Distortions are introduced through a slowly varying displacement field that shifts the positions of each unit cell in the crystal from its perfect-crystal position. The result is a generalization of the Takagi-Taupin equations in the form of a matrix equation for the electric field vector of the X-rays that includes magnetic scattering and the mixing of X-ray polarization states. The solutions of the equations in one-beam and two-beam cases are discussed.

### Introduction

The dominant interaction affecting the propagation of X-rays in matter is Thomson scattering from the constituent electrons. In response to the electric field of the X-rays, the electrons emit dipole radiation with a strength that varies with the scattering direction, depending only on a geometric factor related to the direction of the electric field vector. However, when the X-ray energy is close to the energy difference between occupied and unoccupied electron states within the material, the interaction becomes more complicated. In particular, the presence of these states leads to absorption and changes to the phase of the electromagnetic wave of the X-rays, as characterized by the anomalous-dispersion corrections to the X-ray scattering factors. In many materials, the states available to an electron in an atom depend on the locations of the neighbouring atoms so that the interaction depends on the orientation of the electric field vector of the X-rays (*i.e.* the state of polarization) relative to the neighbouring atoms.

This vector character of the X-ray field provides a useful probe for examining the variation, or anisotropy, of the environment about an atom. The absorption measurements in the EXAFS technique depend on the

direction of polarization of the X-rays (Stern, 1974) and have provided information on the anisotropy in single crystals (Heald & Stern, 1977, 1978; Cox & Beaumont, 1980). The angular dependence of X-ray absorption spectra is discussed in the review by Brouder (1990). Dichroism and birefringence are related effects that occur in anisotropic crystals when the absorption and the refractive index, respectively, depend on the direction of polarization of the waves. Templeton & Templeton (1980, 1982, 1985*a*, 1988, 1989) have observed X-ray dichroism in selected crystals using linearly polarized X-rays and have measured the anisotropy of the anomalous scattering factors near the absorption edges. Similarly, Petcov, Kirfel & Fischer (1990) observed dichroism and birefringence in lithium niobate and developed a model of X-ray transmission based on the elementary optical matrices of Jones (1948).

In X-ray diffraction experiments on anisotropic crystals, the existence of dichroism and birefringence can reduce the degree of symmetry in the crystal and lead to the observation of 'forbidden' reflections. It was predicted by Dmitrienko (1983, 1984) that this would occur for screw axis and glide plane forbidden reflections. It was verified experimentally by Templeton & Templeton (1985*b*, 1987) and Kirfel, Petcov, Fischer & Eichhorn (1989). A theory of kinematical diffraction in anisotropic materials based on Jones's calculus (Jones, 1941, 1948) was developed and tested by Kirfel, Petcov & Eichhorn (1991), Kirfel & Petcov (1992) and Kirfel & Morgenroth (1993).

Although the interaction between the electric field of the X-rays and the charge on the electrons dominates, there are also couplings between the magnetic field of the X-rays and the magnetic moment of the electrons. These additional interactions are observed when X-rays scatter from magnetic materials (de Bergevin & Brunel, 1981). In particular, the electron spin and the orbital magnetic moments in magnetic materials have preferred orientations that introduce anisotropy and lead to X-ray dichroism that can be measured near absorption edges (Schutz *et al.*, 1987). In these materials, additional X-ray optical effects arise, such as the rotation of the plane of polarization (optical activity) and the change in the plane of polarization with the application of a magnetic field

(Faraday effect). These effects were observed by Siddons, Hart, Amemiya & Hastings (1990). The magnetic interaction can lead to a coupling between orthogonal polarization states and it is sensitive to circularly polarized X-rays. X-ray magnetic circular dichroism was used by Wu *et al.* (1993) to investigate oscillations in the magnetic exchange coupling between two ferromagnetic layers. When the X-ray energy is close to the energy difference between electronic states in the crystals, resonantly enhanced magnetic scattering occurs (Namikawa, Ando, Nakajima & Kawata, 1985; Gibbs *et al.*, 1988; Hannan, Trammell, Blume & Gibbs, 1988). This depends on the polarization of the X-rays and provides a sensitive measure of the variation of the density of states above the Fermi level. A general review of polarization phenomena in X-ray optics is given by Belyakov & Dmitrienko (1989). The scattering of photons by magnetic materials is discussed in the reviews by Lovesey (1993) and Lovesey, Kechrakos & Trohidou (1994).

The theories of X-ray scattering in dielectric and magnetic materials differ in their general approach. Dielectric scattering is usually based on a form of Maxwell's equations using either the electric field or the electric displacement of the electromagnetic wave in the crystal. Magnetic scattering is derived from quantum theory and is expressed in terms of a differential cross section. The aim of this paper is to derive a general equation for the interaction of X-rays with anisotropic materials that includes electric and magnetic interactions in a consistent manner. The theory is an extension of the Takagi-Taupin theory (Takagi, 1962, 1969; Taupin, 1964) that contains slowly varying amplitudes to take account of distortions, introduced by strains, and variations in the properties of the crystals, such as the rotations of the direction of magnetization as observed in rare earths (Gibbs, Moncton, D'Amico, Bohr & Grier, 1985; Gibbs, Bohr, Axe, Moncton & D'Amico, 1986; Bohr, Gibbs, Moncton & D'Amico, 1986).

In the following sections, the interaction of the vector potential of the X-rays with the electrons in the crystal is derived using a mixture of classical electromagnetic theory, based on Maxwell's equations, and quantum scattering theory. From Takagi (1962, 1969), the electromagnetic field of the X-rays is expanded in a Fourier series of reciprocal-lattice vectors using Fourier coefficients that are slowly varying functions of position. The interactions of the X-rays with the electrons in the crystal are introduced through scattering factors derived from quantum theory. The effects of distortions in the crystal are included *via* a slowly varying displacement field. The result is a matrix equation that describes the variation and the coupling of the electric field vectors of the X-rays within the crystal. The solutions of the equation for the propagation (one-beam equation) and for the diffraction (two-beam equations) of X-rays in anisotropic materials are discussed.

## Theory

The description of X-ray diffraction from crystals requires a model of the interaction of the electromagnetic field with the atoms in the lattice. The usual formulations follow the classical descriptions of Ewald and Laue (Wagenfeld, 1968). Laue's method is based on a phenomenological macroscopic approach that uses a dielectric susceptibility for the lattice. In anisotropic crystals, this dielectric susceptibility is a tensor that introduces coupling between polarization states (see the review by Kolpakov, Bushuev & Kuz'min, 1978). The natural extension of this to magnetic scattering is achieved with the introduction of the magnetic susceptibility. The problem with this approach is that the classical susceptibilities are based on electric and magnetic dipoles induced by the presence of the X-rays. Gell-Mann & Goldberger (1954) have shown that the scattering of photons from electrons involves not only dipole scattering but a mixture of quadrupole and dipole scattering. To take account of this, an extension of Ewald's approach from classical electron theory to quantum electron theory is useful. This approach was taken by Molière (1939) and, more recently, it was used by Afanas'ev & Kagan (1967) to develop a theory of dynamical X-ray diffraction taking into account inelastic scattering from phonons and by Afanas'ev & Kohn (1971) for X-ray diffraction from distorted dielectric crystals.

The starting point is the wave equation for the vector potential  $\mathbf{A}(\mathbf{r}, t)$ . In the transverse gauge, the components of the vector potential are perpendicular to the direction of propagation of the wave so that

$$\nabla \cdot \mathbf{A}(\mathbf{r}, t) = 0. \quad (1)$$

Then, in Gaussian units, the wave equation has the form (Jackson, 1975)

$$\nabla^2 \mathbf{A}(\mathbf{r}, t) - (1/c^2) \partial^2 \mathbf{A}(\mathbf{r}, t) / \partial t^2 = -(4\pi/c) \mathbf{J}_t(\mathbf{r}, t), \quad (2)$$

where  $\mathbf{J}_t(\mathbf{r}, t)$  is the current density transverse to the direction of propagation of the electromagnetic wave and  $c$  is the velocity of light in vacuum. As a consequence of (1), the vector potential can be represented by a sum of two vectors that are orthogonal to the direction of propagation. The unit vectors in these directions are the polarization vectors,  $\hat{\mathbf{e}}_\alpha$ , where  $\alpha = 1, 2$ .

As in the method of Takagi (1969), the vector wave amplitude can be expanded in a Fourier series of reciprocal-lattice vectors based on the undistorted crystal. The distortions in the crystal structure are assumed to be slowly varying with position and are accounted for by taking the Fourier coefficients as slowly varying functions of position. This method has the advantage of allowing for variations in crystal composition and changes in the X-ray amplitude due to absorption and

*Pendellösung* oscillations. The Fourier expansion is

$$\mathbf{A}(\mathbf{r}, t) = \sum_{g, \alpha} A_{g\alpha}(\mathbf{r}) \hat{\mathbf{e}}_{g\alpha} \exp[-2\pi i(\mathbf{k}_g \cdot \mathbf{r} - kct)], \quad (3)$$

where  $\mathbf{k}_g = \mathbf{k}_0 + \mathbf{g}$  is the wave vector of the Fourier component,  $\mathbf{k}_0$  is the wave vector of the incident X-ray,  $k = |\mathbf{k}_0|$  and  $\mathbf{g}$  is a reciprocal-lattice vector of the undistorted crystal. The sum is over all reciprocal-lattice vectors and polarization vectors.

If this expansion is placed in the wave equation (2) and only first-order variations in the amplitude are returned, the equation takes the form

$$\mathbf{k}_h \cdot \nabla A_{h\alpha}(\mathbf{r}) - i\pi(k_h^2 - k_0^2)A_{h\alpha}(\mathbf{r}) = -(i/cV) \int_V \hat{\mathbf{e}}_{h\alpha} \cdot \mathbf{J}_r(\mathbf{r}, t) \exp[2\pi i(\mathbf{k}_h \cdot \mathbf{r} - kct)] d^3r, \quad (4)$$

where  $A_{h\alpha}(\mathbf{r})$  is approximately constant, *i.e.*  $|\nabla A_{h\alpha}/A_{h\alpha}| \ll k$  over the volume  $V$  of the unit cell. The sum over reciprocal-lattice vectors has been removed by multiplying by  $\hat{\mathbf{e}}_{h\alpha} \exp[2\pi i(\mathbf{k}_h \cdot \mathbf{r} - kct)]$  and integrating over the unit cell at  $\mathbf{r}$ .

The current density arises from the perturbation to the motion of the electrons in the crystal by the electromagnetic field of the X-rays. The perturbation contains linear and non-linear dependences on the X-ray amplitude. Since the non-linear terms are only significant at extremely high flux, only those terms that are linear in the X-ray amplitude will be considered. Then the magnitude and phase of the current density is proportional to the X-ray wave. The slowly varying amplitude  $A_{g\alpha}(\mathbf{r})$  and the time-dependent phase  $\exp[2\pi i kct]$  are factored out of the transverse current in (4), which is replaced by a sum over the electron currents  $\mathbf{J}_{n, \alpha'}$  induced by the unit vector potential  $\hat{\mathbf{e}}_{g\alpha'} \exp[-2\pi i \mathbf{k}_g \cdot \mathbf{r}]$ . Then (4) becomes

$$\mathbf{k}_h \cdot \nabla A_{h\alpha}(\mathbf{r}) - i\pi(k_h^2 - k_0^2)A_{h\alpha}(\mathbf{r}) = -i\pi k^2 \sum_{g, \alpha'} F_{h\alpha h\alpha'}^d(\mathbf{r}) A_{g\alpha'}(\mathbf{r}), \quad (5)$$

where

$$F_{h\alpha g\alpha'}^d(\mathbf{r}) = (1/\pi k^2 cV) \sum_{a, n} \int_V \hat{\mathbf{e}}_{h\alpha} \cdot \mathbf{J}_{n, \alpha'}(\mathbf{r}) \times \exp[2\pi i \mathbf{k}_h \cdot \mathbf{r}] d^3r. \quad (6)$$

The sum is over all electrons,  $n$ , in each atom and over all atoms,  $a$ , in the unit cell. The subscript  $a$  has been omitted for convenience. The function  $F_{h\alpha g\alpha'}^d(\mathbf{r})$  is related by a constant to the structure factor and it is the fraction of the wave  $A_{g\alpha'}(\mathbf{r})$  that scatters into  $A_{h\alpha}(\mathbf{r})$  in the unit cell. For dipole scattering in dielectric materials, it reduces to the Fourier transform of the dielectric susceptibility. The superscript  $d$  signifies that the scattering function is calculated for the distorted crystal.

The integral in (6) has the same form as the classical Hamiltonian for the interaction of the current density  $\mathbf{J}_{n, \alpha'}(\mathbf{r})$  of an electron with an electromagnetic plane

wave of unit amplitude (Flügge, 1971). To account for the interactions properly, this expression is replaced by the equivalent quantum Hamiltonian. Then the scattering function can be expressed as a sum of four terms:

$$F_{h\alpha g\alpha'}^d = -(r_e \lambda^2 / \pi V) \sum_{a, n} (f_n^T + f_n^S + f_n^{A+} + f_n^{A-}), \quad (7)$$

where  $r_e$  is the classical electron radius and  $\lambda = 1/k$  is the X-ray wavelength.  $f_n^T$  and  $f_n^S$  are the first-order scattering amplitudes associated with the interaction between the X-rays and the electron charge density (Thomson scattering) and the electron spin density, respectively. The second-order amplitudes  $f_n^{A+}$  and  $f_n^{A-}$  are the anomalous terms associated with the excitation of the electrons in the material to intermediate states. These terms are given explicitly by Blume (1985) in the non-relativistic limit to order  $(\hbar\omega/mc^2)^2$ :

$$f_n^T = \hat{\mathbf{e}}_{h\alpha} \cdot \hat{\mathbf{e}}_{g\alpha'} \langle B | \exp[2\pi i(\mathbf{h} - \mathbf{g}) \cdot \mathbf{r}_n] | A \rangle, \quad (8)$$

$$f_n^S = (-i\lambda_c/\lambda) (\hat{\mathbf{e}}_{h\alpha} \times \hat{\mathbf{e}}_{g\alpha'}) \cdot \langle B | \exp[2\pi i(\mathbf{h} - \mathbf{g}) \cdot \mathbf{r}_n] \mathbf{s}_n | A \rangle, \quad (9)$$

$$f_n^{A+} = (1/m) \sum_{l, n'} \langle B | H_{nh} | l \rangle \langle l | H_{n'g} | A \rangle / \Delta E^+, \quad (10)$$

$$f_n^{A-} = (1/m) \sum_{l, n'} \langle B | H_{n'g} | l \rangle \langle l | H_{nh} | A \rangle / \Delta E^-, \quad (11)$$

where

$$H_{nh} = (\hat{\mathbf{e}}_{h\alpha} \cdot \mathbf{p}_n + 2\pi\hbar i[\mathbf{k}_h \times \hat{\mathbf{e}}_{h\alpha}] \cdot \mathbf{s}_n) \exp[2\pi i \mathbf{k}_h \cdot \mathbf{r}_n], \quad (12)$$

$$H_{n'g} = (\hat{\mathbf{e}}_{g\alpha'} \cdot \mathbf{p}_{n'} - 2\pi\hbar i[\mathbf{k}_g \times \hat{\mathbf{e}}_{g\alpha'}] \cdot \mathbf{s}_{n'}) \exp[-2\pi i \mathbf{k}_g \cdot \mathbf{r}_{n'}] \quad (13)$$

and

$$\Delta E^+ = E_A - E_l + \hbar\omega - i\Gamma_l/2, \quad (14)$$

$$\Delta E^- = E_A - E_l - \hbar\omega. \quad (15)$$

The sums in (10) and (11) are over the intermediate states  $l$  of the electrons and  $\mathbf{p}$  and  $\mathbf{s}$  are the momentum and spin operators, respectively. A comparison between (8) and (9) shows that the spin-density scattering is smaller than the Thomson scattering by the ratio of the Compton wavelength to the X-ray wavelength,  $\lambda_c/\lambda$ . The anomalous-scattering amplitudes, (10) and (11), contain the effects of electron resonances that occur when the X-ray energy is close to the energy difference between electron states. The factor  $\Gamma_l$  is the resonance width of the intermediate state. These terms represent the excitation of electrons from state  $A$  to an intermediate state  $l$  and the subsequent decay to state  $B$ . The absorbed and emitted X-rays have polarization states that are coupled to the electron momentum and spin.

The anisotropy in the X-ray scattering can be seen explicitly in the equations above. The spin-density scattering (9) depends on the vector direction of the Fourier transform of the electron spin density. This introduces a preferred orientation in the crystal. Unlike the Thomson scattering (8) that is zero for a  $\pi/2$  change in polarization direction on scattering, the spin-density scattering couples orthogonal polarization states *via* the vector cross product. The coupling to the orbital angular momentum of the electrons, as well as additional coupling to the electron spin, is contained in the anomalous terms (10) and (11) and also leads to anisotropy and a coupling between polarization states on scattering. The polarization dependence of the magnetic scattering is discussed by Blume & Gibbs (1988).

Anisotropy also occurs in anomalous scattering by virtue of the orientation dependence of the intermediate electronic states,  $l$ . These states are sensitive to the locations of the neighbouring atoms. The anisotropies associated with EXAFS occur in these terms. The intermediate electron states include those arising from the reflection of the electron waves from the neighbouring atoms (Stern, 1974). The anomalous terms are significant only when  $\Delta E^+$  is small so that the anisotropy is observed only near the X-ray absorption edge. Note that there is the possibility of coupling between orthogonal polarization states of the X-rays by the absorption of one state and the emission of the other state, equations (12), (13) and (10). Enhanced magnetic scattering also results when the X-ray energy is close to the energy difference between electron states (Hannan, Trammell, Blume & Gibbs, 1988).

### Distortions

The effects of lattice distortions introduced by strains are contained implicitly in the scattering function  $F_{h\alpha g\alpha'}^d(\mathbf{r})$  for the distorted crystal. These can be shown explicitly by relating the distorted crystal scattering function to the undistorted crystal scattering function using a displacement field  $\mathbf{u}(\mathbf{r})$ , which is taken as a slowly varying function over each unit cell about  $\mathbf{r}$ . The displacement field shifts the  $n$ th electron from its original position at  $\mathbf{r}'_n$  to  $\mathbf{r}_n = \mathbf{r}'_n + \mathbf{u}(\mathbf{r}'_n)$  in the distorted unit cell. Then the distorted positions  $\mathbf{r}_n$  of the electrons in the phase terms in (8), (9), (12) and (13) can be replaced by  $\mathbf{r}'_n + \mathbf{u}(\mathbf{r}'_n)$ . If  $\mathbf{u}(\mathbf{r}'_n)$  is slowly varying, so that  $|\partial\mathbf{u}/\partial r| \ll 1$ , it may be considered as a constant in each unit cell and it can be removed from the integrations implicit in the matrix elements. Since  $\mathbf{k}_h - \mathbf{k}_g = \mathbf{h} - \mathbf{g}$ , then the scattering function  $F_{h\alpha g\alpha'}^d(\mathbf{r})$  for the distorted crystal takes the form

$$F_{h\alpha g\alpha'}^d(\mathbf{r}) = \exp[2\pi i(\mathbf{h} - \mathbf{g}) \cdot \mathbf{u}(\mathbf{r})] F_{h\alpha g\alpha'}(\mathbf{r}), \quad (16)$$

where  $F_{h\alpha g\alpha'}(\mathbf{r})$  is the scattering function for the undistorted crystal and it is calculated according to (7)–

(11) based on the unstrained lattice. It is still retained as a function of  $\mathbf{r}$  to take into account slow variations in crystal composition or rotations of the magnetization. It has been assumed that the distortions lead to a negligible change in the initial, intermediate and final states of the electrons that appear in (10) and (11).

### General diffraction equation

The general equation for X-ray diffraction is best represented in a matrix form for the two polarization states. Furthermore, with the time dependence given in (3), the electric field is linearly related to the vector potential. Thus define

$$\mathbf{E}_h(\mathbf{r}) = -2\pi i k \begin{pmatrix} A_{h1}(\mathbf{r}) \\ A_{h2}(\mathbf{r}) \end{pmatrix}, \quad (17)$$

then the general matrix equation for X-ray propagation and diffraction in a distorted, anisotropic, dielectric and magnetic crystal is

$$\hat{\mathbf{k}}_h \cdot \nabla \mathbf{E}_h(\mathbf{r}) = -i\pi k \left[ \sum_g \mathbf{F}_{hg}(\mathbf{r}) \mathbf{E}_g(\mathbf{r}) - 2\beta_h \mathbf{E}_h(\mathbf{r}) \right], \quad (18)$$

where  $\hat{\mathbf{k}}_h$  is the unit vector in the direction of propagation,  $\beta_h$  is the resonance parameter,

$$\beta_h = (k_h^2 - k_0^2)/2k^2, \quad (19)$$

and

$$\mathbf{F}_{hg}(\mathbf{r}) = \begin{pmatrix} F_{h1g1}^d(\mathbf{r}) & F_{h1g2}^d(\mathbf{r}) \\ F_{h2g1}^d(\mathbf{r}) & F_{h2g2}^d(\mathbf{r}) \end{pmatrix} \quad (20)$$

is the scattering matrix from  $\mathbf{g}$  to  $\mathbf{h}$ . The off-diagonal terms in (20) are responsible for the mixing of orthogonal polarization states. Differences in the absorption factors appearing in the diagonal terms lead to dichroism. Equation (18) is a generalization of the Takagi-Taupin equations and has a form similar to the matrix equation of Kato (1973).

The solutions to matrix equations, such as (18), are usually obtained by finding some linear transformation that uncouples the components. This means that the equations for the components are independent and can be solved separately. For example, in the theory of two-beam X-ray diffraction from isotropic dielectric crystals, the matrix (20) has zero off-diagonal terms when orthogonal polarization components are chosen, *e.g.*  $\hat{\mathbf{e}}_1 = \sigma$  and  $\hat{\mathbf{e}}_2 = \pi$ . Then the equations are solved for the two polarization states separately.

In the following sections, the equations for the propagation of an X-ray beam through an anisotropic medium (one-beam theory) and the kinematical and dynamical diffraction of the X-rays (two-beam theory) will be considered.

### One-beam equation

For the case where there is no diffraction, the passage of the X-ray through an anisotropic material is described by

$$\partial \mathbf{E}(\mathbf{r}) / \partial s = -i\pi k \mathbf{F}_{00}(\mathbf{r}) \mathbf{E}(\mathbf{r}), \quad (21)$$

where  $s$  represents the distance along the direction of propagation of the beam. This equation has the same form as that for the propagation of light in an optical medium. The various components of  $\mathbf{F}_{00}$  that give rise to absorption, refraction, dichroism and birefringence are analogous to the optical terms summarized by Jones (1948). The form (21) based on the formalism of Jones (1941, 1948) was used by Petcov, Kirfel & Fischer (1990) to describe X-ray birefringence and dichroism in uniform anisotropic materials.

To solve this equation, note that the scattering matrix can be written as the sum of a diagonal matrix  $\Lambda$  and an off-diagonal matrix  $\Gamma$ . Explicitly,

$$\begin{aligned} -i\pi k \mathbf{F}_{00} &= -i\pi k \begin{pmatrix} F_{11} & 0 \\ 0 & F_{22} \end{pmatrix} - i\pi k \begin{pmatrix} 0 & F_{12} \\ F_{21} & 0 \end{pmatrix} \\ &= \Lambda + \Gamma, \end{aligned} \quad (22)$$

where the position dependence is implicit and the  $\mathbf{h} = \mathbf{g} = 0$  subscripts have been omitted for convenience. The important property of these matrices is that the product of two diagonal matrices or the product of two off-diagonal matrices yields a diagonal matrix;  $\Lambda\Lambda$  and  $\Gamma\Gamma$  are diagonal. In terms of  $\Lambda$  and  $\Gamma$ , (21) becomes

$$\partial \mathbf{E} / \partial s = (\Lambda + \Gamma) \mathbf{E}. \quad (23)$$

To remove the off-diagonal matrix, an independent equation is required. This may be obtained by taking a second derivative of (23). Then the diagonal and off-diagonal matrices are separated and  $\partial \mathbf{E} / \partial s$  from (23) is substituted in the off-diagonal term, yielding

$$\partial^2 \mathbf{E} / \partial s^2 = \partial(\Lambda \mathbf{E}) / \partial s + (\partial \Gamma / \partial s) \mathbf{E} + \Gamma(\Lambda + \Gamma) \mathbf{E}. \quad (24)$$

Again using (23), it is possible to write  $\mathbf{E}$  as a function of off-diagonal terms only,

$$\mathbf{E} = \Gamma^{-1} [\partial \mathbf{E} / \partial s - \Lambda \mathbf{E}], \quad (25)$$

since the inverse  $\Gamma^{-1}$  is also an off-diagonal matrix. Then, separation of the diagonal terms from the off-diagonal terms in (24) and substitution of (25) for  $\mathbf{E}$  in the off-diagonal terms yields

$$\begin{aligned} \partial^2 \mathbf{E} / \partial s^2 - \{\Lambda + \Gamma \Lambda \Gamma^{-1} + [\partial \Gamma / \partial s] \Gamma^{-1}\} (\partial \mathbf{E} / \partial s) \\ + \{\Gamma \Lambda \Gamma^{-1} \Lambda - \Gamma^2 + [\partial \Gamma / \partial s] \Gamma^{-1} \Lambda \\ - \partial \Lambda / \partial s\} \mathbf{E} = 0. \end{aligned} \quad (26)$$

The coefficients in this equation are all diagonal. Its solution is not possible for arbitrary variations of the scattering matrix but for constant coefficients it simpli-

fies to

$$\begin{aligned} \partial^2 \mathbf{E} / \partial s^2 + i\pi k (F_{11} + F_{22}) \partial \mathbf{E} / \partial s \\ - \pi^2 k^2 (F_{11} F_{22} - F_{12} F_{21}) \mathbf{E} = 0 \end{aligned} \quad (27)$$

for both polarization modes. The solution of this equation is straightforward:

$$\mathbf{E}(s) = \mathbf{A} \exp[-i\pi k \eta^+ s] + \mathbf{B} \exp[-i\pi k \eta^- s], \quad (28)$$

where

$$\eta^\pm = (F_{11} + F_{22}) / 2 \pm ([F_{11} - F_{22}]^2 + 4F_{12}F_{21})^{1/2} / 2 \quad (29)$$

and  $\mathbf{A}$  and  $\mathbf{B}$  are constants determined by the vector amplitude at  $s = 0$ .

The solution (28) with definition (29) has a simple interpretation. The refractive index of the medium is given by  $n = 1 + \eta/2$ , provided  $\eta \ll 1$ . Thus,  $\eta$  is twice the change in the refractive index of the medium relative to the vacuum. The first term in (29) represents the effects of an average refractive index of the medium that induces a phase shift in the propagating wave relative to the vacuum wave. The second term results from the anisotropy of the crystal that splits the wave into two components that propagate with differing phase velocities.

### Two-beam equations

If the incident beam scatters into a single diffracted beam, then (18) decomposes into coupled equations for the two vector amplitudes

$$\partial \mathbf{E}_0 / \partial s_0 = -i\pi k (\mathbf{F}_{00} \mathbf{E}_0 + \mathbf{F}_{0h} \mathbf{E}_h), \quad (30)$$

$$\partial \mathbf{E}_h / \partial s_h = -i\pi k ([\mathbf{F}_{hh} - 2\beta_h] \mathbf{E}_h + \mathbf{F}_{h0} \mathbf{E}_0), \quad (31)$$

where  $s_0$  and  $s_h$  represent the distances travelled by the incident X-rays and the diffracted X-rays, respectively. The equations can be decoupled in the usual way by taking second derivatives. For example, the derivative  $\partial^2 \mathbf{E}_0 / \partial s_h \partial s_0$  is formed from (30), (31) is substituted for  $\partial \mathbf{E}_h / \partial s_h$  and  $\mathbf{E}_h$  is substituted by a rearrangement of (30). This yields

$$\begin{aligned} \partial^2 \mathbf{E}_0 / \partial s_h \partial s_0 = -i\pi k \partial (\mathbf{F}_{00} \mathbf{E}_0) / \partial s_h + \mathbf{M}_0 \partial \mathbf{E}_0 / \partial s_0 \\ + (i\pi k \mathbf{M}_0 \mathbf{F}_{00} - \pi^2 k^2 \mathbf{F}_{0h} \mathbf{F}_{h0}) \mathbf{E}_0, \end{aligned} \quad (32)$$

where

$$\mathbf{M}_0 = [\partial \mathbf{F}_{0h} / \partial s_h - i\pi k \mathbf{F}_{0h} (\mathbf{F}_{hh} - 2\beta_h)] \mathbf{F}_{0h}^{-1}. \quad (33)$$

Similarly,

$$\begin{aligned} \partial^2 \mathbf{E}_h / \partial s_0 \partial s_h = -i\pi k \partial ([\mathbf{F}_{hh} - 2\beta_h] \mathbf{E}_h) / \partial s_0 + \mathbf{M}_h \partial \mathbf{E}_h / \partial s_h \\ + [i\pi k \mathbf{M}_h (\mathbf{F}_{hh} - 2\beta_h) - \pi^2 k^2 \mathbf{F}_{h0} \mathbf{F}_{0h}] \mathbf{E}_h, \end{aligned} \quad (34)$$

where

$$\mathbf{M}_h = [\partial \mathbf{F}_{h0} / \partial s_0 - i\pi k \mathbf{F}_{h0} \mathbf{F}_{00}] \mathbf{F}_{h0}^{-1}. \quad (35)$$

The various terms in (32) and (34) can be interpreted in terms of the interactions in the crystal. The first term on the right of (32) represents the propagation of the wave through the anisotropic medium, in a similar fashion to the one-beam case, equation (21). The second and third terms represent the effects of the coupling of the transmitted wave on the diffracted beam that is propagating in the anisotropic medium, while the last term arises from the dynamical scattering of the incident beam into the diffracted beam and back again. A similar interpretation can be applied to (34). Note that the  $F_{00}$  and  $F_{hh}$  terms are analogous to the refractive-index term  $\chi_0$  in an isotropic dielectric medium. Often  $\chi_0$  is included with the X-ray wave number (Takagi, 1969) leading to simpler expressions for the diffraction equations. This is no longer possible since  $F_{00}$  and  $F_{hh}$  are matrices that couple different polarization states.

Although (32) and (34) are no longer coupled in the wave amplitudes, there still remains coupling between polarization states. This creates difficulties in obtaining analytical solutions except under certain conditions, such as slab geometry and constant coefficients. Solutions in this case are discussed in a review of the diffraction of *Mössbauer*  $\gamma$ -rays in crystals by Belyakov (1975). Solutions may also be obtained by numerical evaluation of (30) and (31).

In the case of kinematical scattering, the coupling coefficient  $F_{0h}$  in (30) is neglected. For isotropic dielectric crystals, this results in an incident wave amplitude that is constant or that is attenuated with distance in the crystal by absorption. However, in anisotropic crystals, the incident wave amplitude varies according to (21), so there is the added complication that different polarization states of the incident beam may be propagating with different phase velocities and they may be coupled. The kinematical scattering at any point in the crystal will depend on the state of the incident beam at that point. Therefore, even the general kinematical solution is complicated. In the case where the matrix  $F_{hh}$  is constant, the kinematical solution can be obtained by finding a transformation matrix  $T$  that diagonalizes  $F_{hh} - 2\beta_h$ ,

$$\mathbf{T}^{-1}(\mathbf{F}_{hh} - 2\beta_h)\mathbf{T} = \Lambda_h, \quad (36)$$

where  $\Lambda_h$  is a diagonal matrix. The solution of (36) for  $T$  and  $\Lambda_h$  is a standard eigenvalue problem. The kinematical solution of (31) is then

$$\begin{aligned} \mathbf{E}_h(s_h) = & -i\pi k \mathbf{T} \exp[-i\pi k \Lambda_h s_h] \\ & \times \int_0^{s_h} \exp[i\pi k \Lambda_h s] \mathbf{T}^{-1} \mathbf{F}_{h0}(s) \mathbf{E}_0(s) ds, \end{aligned} \quad (37)$$

where the integration is along the path of the diffracting

beam. This equation is valid provided the scattering is weak. Since magnetic scattering factors are smaller than the Thomson scattering factor by about two orders of magnitude, then (37) should be valid for analysing magnetic scattering experiments when the Thomson scattering can be treated kinematically.

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## Diffraction by Aggregates of Helical Molecules

BY R. P. MILLANE AND W. J. STROUD

*Whistler Center for Carbohydrate Research, Purdue University, West Lafayette, IN 47907-1160, USA*

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### Abstract

An expression is derived for the intensity diffracted by a non-crystalline fiber made up of aggregates of helical molecules. This expression is useful for the efficient calculation of diffraction from such specimens and provides insight into the effects of aggregation on diffraction patterns. Example calculations show a number of implications for structure determination.

### 1. Introduction

X-ray fiber diffraction is used to determine the structures of polymers and other macromolecules that exist naturally as, or can be prepared as, oriented fibers or planar arrays (Millane, 1988). The molecules themselves usually adopt helical structures. In some specimens, the molecules are merely oriented with their long axes approximately parallel and are randomly rotated about these axes (Namba & Stubbs, 1985; Bhattacharjee, Glucksman & Makowski, 1992). In others, the molecules further organize laterally into very small crystalline regions and the orientations of the crystallites about the long axes of the constituent molecules are random (Leslie, Arnott, Chandrasekaran & Ratliff, 1980). These are referred to as non-crystalline and polycrystalline specimens, respectively. Specimens exhibiting ordering intermediate between these two extremes also exist (Millane & Stroud, 1991). Structure determination involves calculation of the intensity diffracted by the specimen and, in the case of a non-crystalline fiber, this is equal to the cylindrical average of the intensity of the Fourier transform of one molecule.

Other cases occur, however, where two or more helical molecules aggregate in a specific manner to form the fundamental particles that are randomly rotated in a fiber

specimen. The intensity diffracted by the specimen is then related to the Fourier transform of the aggregate structure, which sometimes can be a computationally intensive calculation. The objective of this paper is to derive an expression for the intensity diffracted by such a specimen, in terms of the Fourier transform of a single molecule and the geometric relationships between the molecules. This provides a substantial decrease in the amount of computation required, compared to a calculation directly from the aggregate structure, and provides insight into differences in the diffraction by independent and by aggregated molecules.

There are a number of macromolecular systems that exhibit this kind of aggregation, for which these results might be useful, and some examples where X-ray fiber diffraction has been used to derive structural information are as follows. Nucleic acids form double- and triple-stranded molecules that are made up of two or three (almost) identical strands (Leslie, Arnott, Chandrasekaran & Ratliff, 1980; Park, Arnott, Chandrasekaran, Millane & Campagnari, 1987), and polysaccharides such as carrageenans and gellan form double helices (Millane, Chandrasekaran, Arnott & Dea, 1988; Chandrasekaran, Millane, Arnott & Atkins, 1988). Aggregates of polysaccharide helices formed by lateral associations have also been considered (Paoletti, Cesaro & Delben, 1983). Collagen triple helices have a high potential for lateral interactions and form a variety of microfibrillar and fibrillar aggregates (Fraser, MacRae & Miller, 1987; van der Rest & Garrone, 1991; Kajava, 1991). The deoxygenated form of sickle-cell hemoglobin molecules polymerize into long strands, and these form dimers by side-by-side association, followed by alignment and lateral aggregation of the dimers to form fibers and macrofibers with specific lateral interactions (Magdoff-Fairchild & Chiu, 1979; Potel, Wellems, Vassar, Deer &